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## A SINGLE-CRYSTAL MICROBEAM X-RAY GONIOMETER<sup>1</sup>

By JOSEPH SINGER<sup>2</sup>, JOHN A. RICHARDS, AND WILLIAM C. MOXLEY

### ABSTRACT

A microbeam X-ray diffraction camera has been built for irradiation of selected areas of  $\sim 35 \mu$  diameter. The instrument is designed about a horizontal Machlett diffraction tube, but can be used with other, including high intensity, installations. Single crystal oscillation and Laue techniques are provided for, a special centered goniometer head being included. Lead-glass collimators are used for defining the beam, and location of the latter is achieved with a fluorescent crystal and a Geiger counter.

X-ray diffraction microcameras and associated X-ray microbeam techniques have recently been receiving increased attention (1, 3, 4, 5, 6) although the essential ideas are not new (7, 8, 9). Generally, the microarea has been selected and irradiated by fastening the specimen to the collimator under a microscope. Recent developments (1, 2, 3, 4, 5) have been in the direction of mounting the collimator and specimen independently. This technique was used in the camera described here in order to remove restrictions upon the nature and environment of the specimen. Collimation has usually been accomplished by means of lead-glass capillaries (3, 4, 5, 6). The instrument described has as yet been used with beams no smaller than  $35 \mu$  in diameter, although this is not a lower limit inherent in the design. Special high-intensity X-ray sources have not yet been employed, although this logical development (4, 5, 6) is planned for the future.

As reported earlier (10), the camera consists essentially of three principal assemblies; a collimator, a goniometer with a crystal-mounting head, and a microscope. Fig. 1 shows the complete instrument in place on a standard track with a horizontally mounted X-ray tube. The location problems are: (1) to obtain the beam of maximum intensity through the collimator; (2) to align the microscope axis into coincidence with the direction of the X-ray beam; and to place the axis of the goniometer head and the centers of its arcs (the position desired for selected microareas in specimens) in the common line of the X-ray beam and the microscope axis. In the actual alignment procedure, however, a dummy fluorescent specimen mounted on the goniometer head is

<sup>1</sup> Manuscript received March 24, 1953.

Contribution from the University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

<sup>2</sup> Present address: Sylvania Electric Products Co., Bayside, Queens, N.Y.

first brought into the line of the microscope axis; this relationship of microscope to goniometer head and specimen in then preserved while the microscope axis and the direction of the X-ray beam are made coincident, utilizing the fluorescence for this purpose.

Before presenting the alignment procedures, several relevant features of the camera will be discussed. In order to attain maximum versatility with

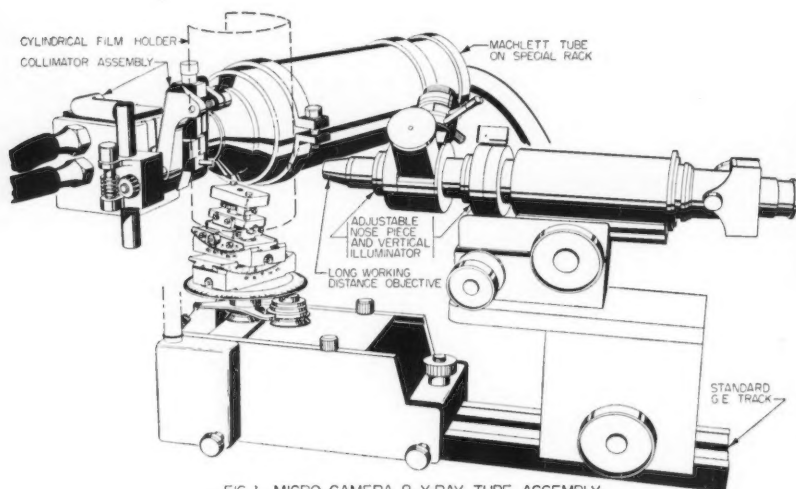


FIG 1 MICRO CAMERA & X-RAY TUBE ASSEMBLY.

single-crystal areas, a special goniometer head was built. This head (Fig. 2) has two lateral drives and a vertical adjustment above the arcs. This design, in conjunction with the feature that the two arcs were made concentric at the same point on the axis of rotation, makes it possible to keep a selected specimen area centered during orientation adjustments. The precision of this maintenance of centering is about  $5\mu$ . The vertical adjustment assembly of the goniometer head is made of Invar, for use with a microfurnace, and the remainder of the head is stainless steel. Either complete rotation of the specimen or cam-controlled oscillations may be obtained.

Other features of the goniometer assembly are: (1) either a semicylindrical cassette or a flat cassette for front reflection may be used; (2) the rotation axis may be moved slightly by screws bearing on the track; and (3) a standard crystal-mounting head may be substituted for the goniometer head simply by adapting a special shaft to the main bearing.

As a temporary expedient, the adjustments of a standard camera track have been employed for controlling movement of the combined goniometer and microscope assemblies. A specially designed track would be desirable. Additional adjustments were provided in the rack supporting the X-ray tube.

The collimator assembly (Fig. 3) is attached to the X-ray tube and has four



screw-driven adjustments. These provide two rotational and two translational motions for the collimator. The collimator is sealed into the assembly with an ethyl cellulose cement containing lead oxide to prevent leakage of radiation along its exterior. As a further precaution against stray radiation the collimator assembly was wrapped with lead foil.

The alignment procedure is as follows. (1) Obtaining a beam. The screw drives on the collimator assembly are used to obtain the strongest beam

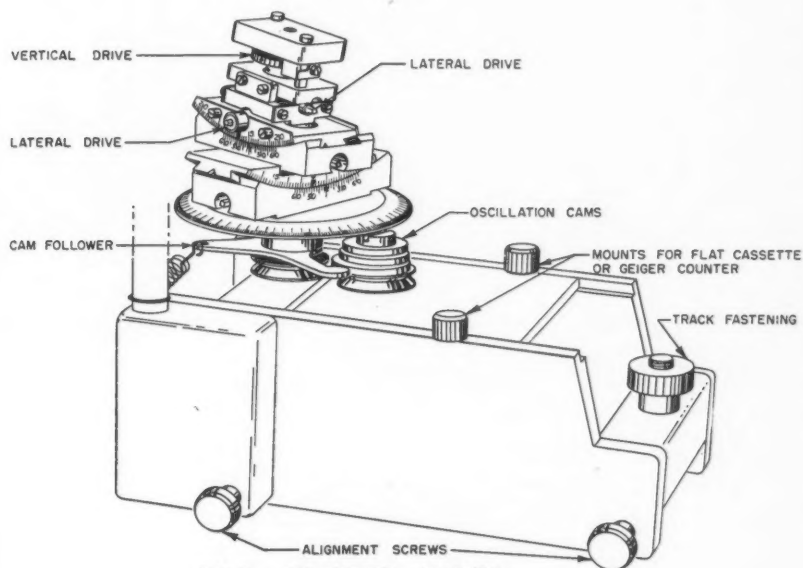


FIG. 2 GONIOMETER ASSEMBLY.

through the leaded-glass capillary, first as observed with a fluorescent screen, and then as indicated by a Geiger counter. Each screw drive is locked at the optimum setting. (2) Setting the axis of rotation and the centers of the goniometer arcs at the cross hair of the microscope. This procedure requires that the microscope objective be adjustable with respect to centering. Coarse adjustment of the height of the microscope, if required, can be made with shims in the microscope mount. The common center of the arcs is found by placing a small specimen on the axis of rotation and adjusting its height on the goniometer head until no movement is observed for full displacement of the arcs, either separately or in combination. Adjustments at the base of the goniometer assembly, together with adjustment of the centering of the microscope objective, are now used to bring this 'camera center' (the center of the arcs) to the intersection of the microscope cross hairs. (3) Pointing the collimator at the camera center and making the beam coaxial with the microscope.

A small fluorescent crystal fragment has been found satisfactory for alignment of beams over  $35\ \mu$ . A row of such fragments is distributed along a thin glass fiber, and one of them is placed at the camera center, as if it were a diffraction sample. By means of the track adjustments and the drive on the X-ray tube rack, the beam from the collimator is caused to illuminate the crystal. To obtain approximate coaxiality of the collimator and microscope, one must be able to see also the end of the collimator at the cross hair simply by advancing

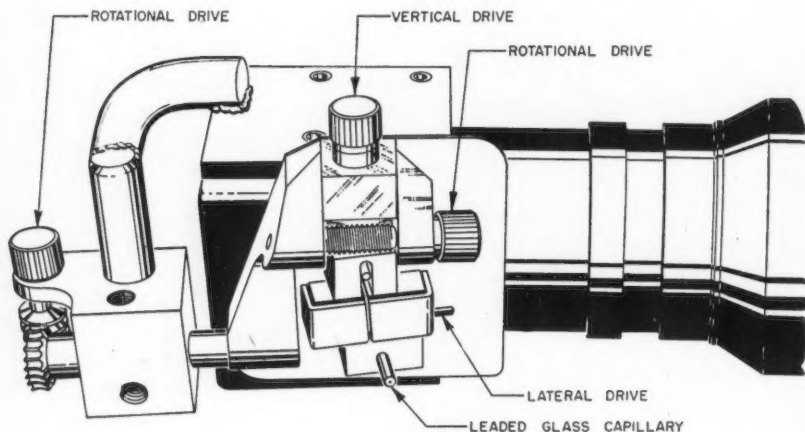


FIG. 3 COLLIMATOR ASSEMBLY.

the microscope. A long working distance type of objective is necessary in order that at a magnification of  $100\times$  it may be advanced to focus on the collimator without striking the specimen. The vertical, horizontal, and rotational adjustments of the standard camera track were used with little modification to obtain this alignment. It is this operation in particular which would be greatly facilitated by a specially designed camera track. For beams appreciably smaller than  $35\ \mu$ , the fluorescent fragment would not provide a sufficiently precise alignment; however other calibration methods are readily devised. For example, the 'sample' could be a small hole in gold or lead foil, with a Geiger counter behind it.

A  $35\ \mu$  beam diffracted from the thin edge of a fragment of  $\text{AuAl}_3$  (cubic) gave a heavily exposed  $15^\circ$  oscillation pattern after about one hour. The copper tube was operating at 35 kv. and 20 ma., and the distance between the specimen and the X-ray tube port was 2.5 cm. The camera has been used with a microfurnace at  $300^\circ\text{C}$ . enclosing the specimen on the goniometer head. It is planned to use the camera for identification of inclusions and other microstructures in polished metallurgical samples by diffraction at glancing incidence.



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## AN INSTRUMENT FOR THE MEASUREMENT OF DISTINCTNESS-OF-IMAGE GLOSS<sup>1</sup>

BY W. E. KNOWLES MIDDLETON<sup>2</sup> AND A. G. MUNGALL<sup>2</sup>

### ABSTRACT

The type of gloss known as distinctness-of-image gloss, which controls the sharpness of images seen in a reflecting surface, has hitherto resisted instrumental measurement. An instrument has been developed for this purpose, essentially an automatic goniophotometer which scans rapidly over a small range of angles centered on the angle of specular reflection, and by electronic means measures the maximum slope of the goniophotometric curve. The meter readings given by this instrument correlate well with the judgments of observers who use no optical aids. The principle of the instrument is the subject of a patent application.

### INTRODUCTION

The term "gloss" is very difficult to define. Several different types of gloss exist and may be described as follows:\*

1. Specular or objective gloss—the ratio of the light reflected by the test surface at the angle of specular reflection to that from a standard specular reflecting surface under the same conditions.
2. Contrast or subjective gloss—the ratio of light scattered specularly to that scattered in some other specified direction.
3. Sheen—the slight increase in surface brightness observed when a matt surface is viewed at almost grazing angle.
4. Bloom—a "spilling-over" of light from highlights reflected in the surface.
5. Surface texture—hardly a gloss property, but closely connected with the observer's impression of gloss.
6. Distinctness-of-image gloss—the sharpness of images viewed in the reflecting surface.

As the reflecting surface observed approaches the uniformity of a mirror, the distinctness-of-image gloss becomes the gloss property which leads the observer to attribute a certain quality of gloss to the surface. With the exception of bloom the other types of gloss, though important for surfaces giving poor image formation, become practically negligible at this point. Consequently, in the quality control of processes producing highly reflecting, uniform plated and painted surfaces, distinctness-of-image gloss is a property of the surface which is of considerable importance to the manufacturer.

The visual evaluation of this type of gloss is complicated by the interference of all the other types, especially bloom and contrast gloss. A number of methods of measuring it and ascribing a numerical scale to it have been suggested, but most of them depend on visual comparison with standards (see Ref. 1, p. 110), or resolution of the reflections of gratitudes at given angles. It has been found,

<sup>1</sup>Manuscript received April 24, 1953.

Contribution from the Division of Physics, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 3031.

<sup>2</sup>Physicist.

\*Harrison, V. G. W. *Definition and measurement of gloss*. W. Heffer and Sons, Ltd., Cambridge, England, 1945. p. 49ff. This book contains an extensive bibliography.

however, that the order of increasing distinctness-of-image gloss for a series of gloss specimens as deduced by the use of resolving power targets does not correspond with that deduced by simple viewing of the "clearness of reflection" of a single dark bar or a grating of constant size.

On the assumption that the clearness of reflection might be a function of the slope of the illumination curve across the edge of an image formed by focussing the light from an illuminated object reflected by the test surface, an instrument was designed and built which accurately measures this slope and gives a direct indication of the distinctness-of-image gloss of the surface as a deflection on a meter. Close agreement was obtained with visual results for several observers, who used the clearness of reflection of a dark object as their criterion, and it was found that in some cases the instrument was able clearly to distinguish between samples indistinguishable to the observers.

#### PRELIMINARY EXPERIMENTS

Before the instrument was built, we made a close examination of the type of illumination curve that exists across an image formed of the light from an illuminated object reflected by various glossy surfaces. The object consisted of a straight edge (razor blade) fixed to the flashed surface of a strongly illuminated piece of opal glass. The light from this object was reflected from the test surface at an angle of  $45^\circ$  and was imaged by a four-element, highly corrected enlarging lens at a magnification of 1:1 on the plane of a travelling slit. Behind this slit, and stationary with respect to it, was placed a photomultiplier tube. The output of the photomultiplier was indicated directly on a recording millivoltmeter, and the slit was motor-driven across the image at constant speed. Slit widths of 10 to  $100\mu$  were used and it was found that diffraction and the residual aberrations of the lens were the limiting factors in determining the slope of the curves. The minimum necessary slit width was thus found to be about  $50\mu$  ( $\sim .002$  in.).

Five sets of gloss samples, each set of a different color and consisting of seven steps of gloss, were examined in the above manner and the slopes of all the illumination curves measured. The sets were then placed in order of increasing distinctness-of-image gloss, evaluated visually by the observation of the reflection of a bar, and this order was compared with that found by the criterion of increasing maximum slope of the illumination curves. With a few exceptions, the two orders were identical. These exceptions occurred only when the sample in question displayed very poor distinctness-of-image gloss, and were thus probably due to the interfering effects of contrast gloss and bloom. The latter effects appeared on the illumination functions as very gradual "tailing out" of the function at the top and the bottom. For surfaces such as these, distinctness-of-image gloss is obviously subordinate to contrast gloss and bloom. Consequently we concluded that although the slope of the illumination curve may be a questionable measure of distinctness-of-image gloss for relatively dull surfaces, it would appear to be a good measure for high gloss paint samples and plated surfaces.

## DESIGN AND OPERATION OF THE INSTRUMENT

A simple, rapid method of measuring the slope of the illumination curve was required. This was provided as follows (Fig. 1): Light from the source, S, uniformly illuminates the object A-B, consisting of two sharp slit jaws. It is then reflected at  $45^\circ$  from the test surface X and is focussed by the lens L on

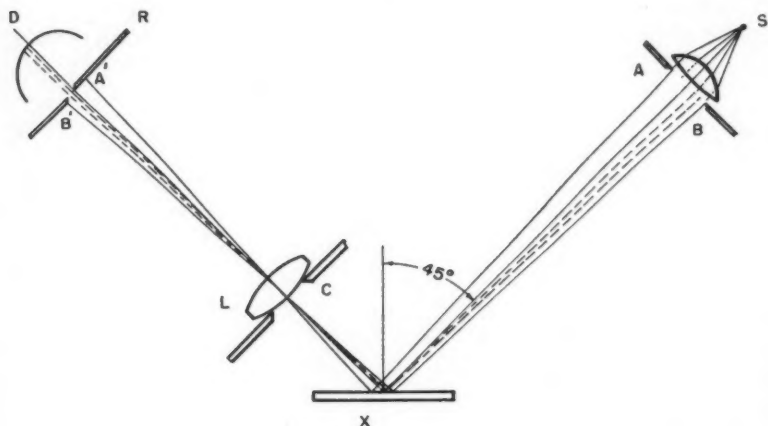


FIG. 1. Illustrating the principle of the new glossmeter.

to the plane of a disk R, rotating at 1800 r.p.m. and containing 23 identical adjustable slits whose jaws are on radii. The light passing through a slit falls on the cathode of a 922 phototube D. The jaws of the object A-B are so oriented that their images A'-B', for perfect reflection by X, fall along radii of the disk R. Consequently, the photocurrent of D will, for a suitably narrow scanning slit, reproduce on a uniform time scale the illumination function across the image A'B'. The optimum value of the slit width is determined by diffraction and lens aberrations, and was about 0.005 in. for the cheaper, simple lens used in the glossmeter. Thus, Fig. 2a represents the function and its time derivative for a perfect reflector, the dotted line being the actual illumination function neglecting lens aberrations or any diffraction effects. Fig. 2b represents typical curves for a glossy paint sample. Actually, since the frequency response of the electronic circuits was not constant for all frequencies, and as neither the illumination across the object nor the sensitivity of the cathode of the 922 were perfectly uniform, the wave forms were somewhat distorted from these ideal shapes. This distortion, however, was not sufficient to affect the results seriously. If in Fig. 2a and 2b the amplitudes of the two square waves are both  $V_0$ , then the amplitude  $pV_0$  and  $qV_0$  of the differentiated waves will be direct measures of the maximum slopes of the curves. In the case shown,  $p$  will obviously be greater than  $q$ .

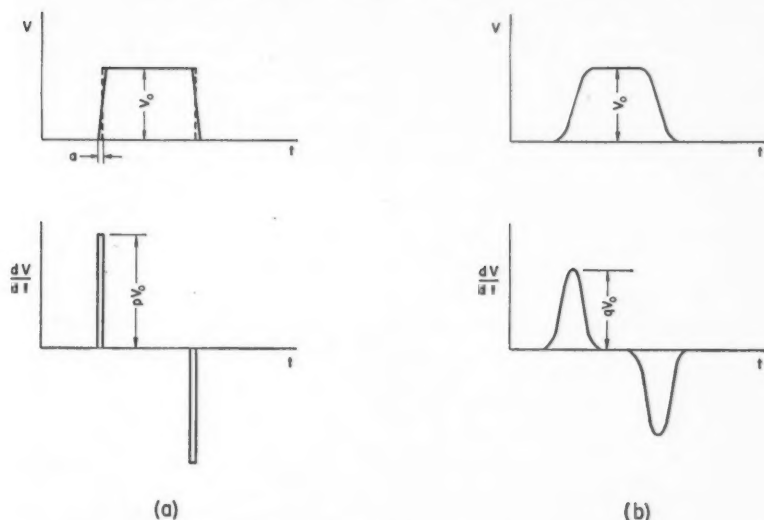


FIG. 2. Direct and differentiated goniophotometric curves.

In the experimental model, the photocurrent develops a voltage across  $R_1$  (Fig. 3), a portion of which is selected and amplified by the first 6AU6. The output is then either attenuated by the  $R_9$ - $R_5$  network by closing the switch in the upward direction, or differentiated by the network  $C_6$ - $R_5$  by closing the switch in a downward direction. The output of either network is then amplified by the second 6AU6 and the amplified voltage measured on the VTVM. The attenuator was constructed so that the meter deflections, proportional to the peak values of the amplified and differentiated wave forms, were of the same order of magnitude and could thus be used on the same VTVM scale.

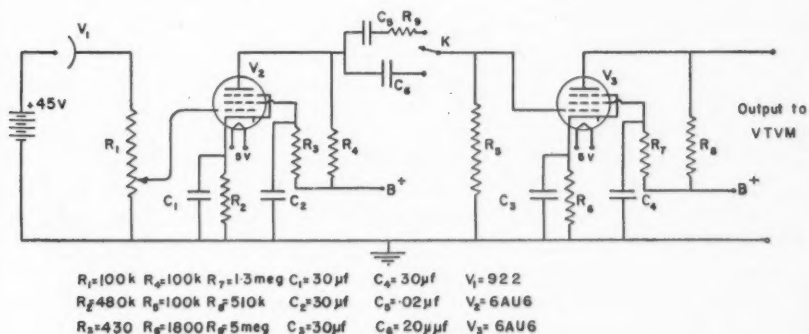


FIG. 3. Diagram of the amplifying and differentiating circuits.

In Fig. 4 is shown an interior view of the glossmeter. The 6 volt projection lamp S is the source of light; the object slit is inside the tube at O. The test sample is clamped firmly in position at X so that the reflected beam of light passes through the simple lens L and is imaged on the motor-driven disk at D. The transmitted light then falls on the phototube P whence the photocurrent passes from the main box to the amplifying and differentiating circuit A. The photocurrent then passes from the main box to the amplifying and differentiating circuit A.

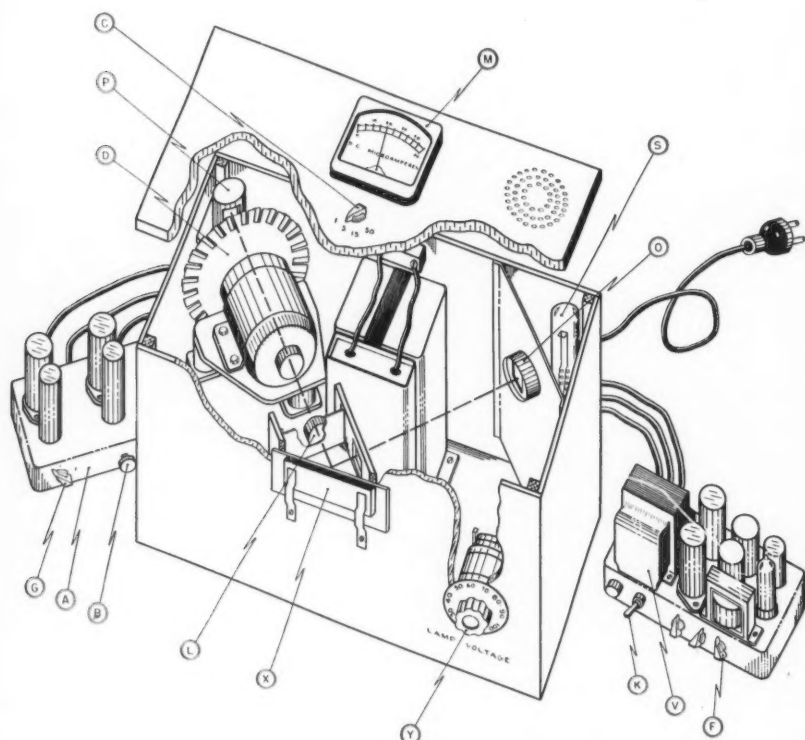


FIG. 4. General view of the glossmeter.

The output of this circuit is then fed into the combination voltmeter and power supply unit V, and the rectified d-c. voltage registered by an open scale microammeter M placed in a convenient position on the lid of the main box. All parts of the electronic circuit are thoroughly shielded to reduce noise to a minimum and prevent oscillations in the amplifier. Four scales of sensitivity are available in the ratios 1, 5, 15, 50 by positioning a selector switch C. The intensity of illumination of the object, and hence the magnitude of  $V_0$ , is adjusted to a suitable value by the variac Y.



The method of making a measurement on a series of samples is as follows: First, with the variac set at zero and the meter on its lowest sensitivity (50), the circuit is turned on and allowed to warm up for 5 or 10 min. Next, the standard of gloss is chosen; for paint samples a flat, polished piece of black glass is suitable, and for plated surfaces, an aluminized glass mirror, front coated. If paint samples are to be measured the amplifier gain  $G$  is set at position 2, and if plated samples, at position 1. The standard is then placed over the test aperture, the zero set by controls on the V.T. voltmeter, and the sensitivity set on the 5 scale. The switch  $K$  is depressed to differentiate the incoming signal. Then the lamp voltage is increased until the value of the differentiated voltage, or figure of merit of the surface indicated by the meter, attains 50. The button  $B$  is then released in order to obtain the value of  $V_0$  (Fig. 2) indicated on the meter. If the sensitivity is not suitable for accurate adjustment of the variac, the amplifier gain  $G$ , or the meter sensitivity  $F$  may be altered. For very large sensitivity changes, the selector switch may be reset. If the sensitivity is changed the zero must be reset, and for positions of very high gain, and high sensitivity, the zeros for the two positions of the button  $B$  may be appreciably different. They should always be checked in any case. To test a sample, the standard is replaced by the sample, the variac adjusted until the meter reads  $V_0$ , the button  $B$  depressed, and the distinctness-of-image gloss (D.I.G.) read directly on  $M$ . Every 10 or 15 min., it is advisable to readjust the zeros, although the drift should not be greater than 0.2 or .3  $\mu$  amp. in that time. Best results are obtained if the 110 volt power supply is regulated, since a small voltage variation produces a large variation in the luminous output of the lamp, both in amount and spectral distribution.

#### TESTS OF THE INSTRUMENT

The five sets of colored gloss samples mentioned in the preliminary experiments were examined by the gloss meter and a satisfactory spread of values of D.I.G. was obtained. As previously, some of the dull samples gave values that did not agree with visual classification. In order to test the instrument more thoroughly we attempted to produce specimens with more suitable ranges of gloss in both paints and metals.

The most satisfactory methods of production of glossy metal surfaces consisted of buffing nickel-plated brass surfaces which had been finished to a desired surface texture before plating, and of electropolishing stainless steels. Not a very wide nor uniform range of gloss was obtainable, but for flat samples, visual classifications agreed with the figures of merit. We had more success with samples made by spraying an enamel or lacquer onto flat glass plaques. Twelve black samples were prepared in this way, all of slightly different distinctness-of-image gloss.

In addition, a series of 14 samples of five different colors (red, blue, gray, white, and black), which had been measured on a standard 60°-60° glossmeter, were selected for us by the Protective Coatings Section of the Division of Applied Chemistry. These were ordinary paint panels which had been prepared for other purposes.

Let us first deal with the black samples, which were evaluated by one observer (A.S.) on three occasions, two more on two occasions each, and once by a fourth observer. There was an interval of at least an hour between the various attempts by the same observer. The observers worked in front of a window with vertical and horizontal sash bars approximately one inch wide, the samples being laid horizontally on a table in such a position that the angles of incidence and of view were about  $45^\circ$ .

Table I shows rank-difference correlation coefficients  $\rho$  (Spearman)\* between the indications of the glossmeter and the estimates of the observers, and also between the pairs of estimates by each observer. It will be seen that these are all high and of much the same magnitude.

TABLE I  
DISTINCTNESS-OF-IMAGE GLOSS METER  
Twelve black samples (paint)  
Rank-difference correlation coefficients

Observer	New glossmeter and observers	Two attempts of each observer
AS(1)	0.99	0.94
AS(2)	0.88	
AS(3)	0.92	
AM(1)	0.91	0.91
AM(2)	0.88	
HB(1)	0.85	0.87
HB(2)	0.77	
HF	0.88	

Next the 14 colored samples were dealt with in a similar way, this time twice by each of four observers, with the results shown in Table II. In this table we have also given the value of  $\rho$  between the observers' estimates of distinctness-of-image gloss and the values of  $60^\circ$ - $60^\circ$  gloss measured on an ordinary gloss meter. It is obvious that  $60^\circ$ - $60^\circ$  gloss does not correlate at all well with D.I.G., but that the readings of the new instrument are much better in this regard.

The experimental work described above was completed just before the appearance of the important paper by Nimeroff (1), in which he shows that the kurtosis index of the goniophotometric curve correlates extremely well with subjective estimates of the distinctness-of-image gloss. We may suppose that the maximum slope of the goniophotometric curve will correlate fairly well with its kurtosis index, so that the present instrument affords an automatic approximation to this quantity. Nimeroff also finds that  $60^\circ$ - $60^\circ$  gloss correlates poorly with distinctness-of-image gloss, especially for dark samples.

\*See, for example, J. P. Guilford. *Psychometric methods*. McGraw-Hill Book Company Inc., N.Y. and London. 1936. p. 339.

TABLE II  
DISTINCTNESS-OF-IMAGE GLOSS METER  
Fourteen multicolored samples (paint)  
Rank-difference correlation coefficients

Observer	New glossmeter and observers		60°-60° Glossmeter and observers
AS(1)	0.82	0.99*	0.44
AS(2)	0.87		0.51
WM(1)	0.92	0.89*	0.58
WM(2)	0.85		0.51
DT(1)	0.91	0.94*	0.51
DT(2)	0.93		0.66
AM(1)	0.81	0.88*	0.36
AM(2)	0.93		0.51

\*These coefficients are between the two attempts of each observer.

#### CONCLUSIONS

It may be concluded that the new instrument actually does measure a property of the goniophotometric curve which correlates fairly well with subjective measurements of D.I.G. The rather rough prototype could probably be improved a good deal. It is, however, limited to specimens that are substantially flat, a restriction shared by most other glossmeters.

A patent application has been filed.

#### ACKNOWLEDGMENT

We wish to acknowledge the kindness of Mr. J. Harris of the Division of Applied Chemistry in providing specimens.

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# LIGNINSULPHONIC ACIDS AS ION-EXCHANGE REGENERANTS<sup>1</sup>

BY B. L. TURVOLGYI, L. ANYAS-WEISZ, AND W. F. GRAYDON

## ABSTRACT

Mixed bed ion-exchange columns can be regenerated without separation by prior regeneration of the anion-exchange resin with sodium hydroxide solutions and subsequent regeneration of the cation-exchange resin with ligninsulphonic acid solutions. The large ligninsulphonate anions exchange very slowly. Data are reported for regeneration level and leakage of ligninsulphonic acids in the regeneration of a cation-exchange resin and for exchange of ligninsulphonic acids on an anion-exchange resin.

## INTRODUCTION

It has been reported (1) that pectic acid solutions may be used to regenerate mixed bed ion-exchange systems without separation. This communication presents data for the similar use of high molecular weight acids derived from sulphite waste liquor, for simplicity designated ligninsulphonic acids.

## EXPERIMENTAL

### *Preparation of Ligninsulphonic Acids*

The cations present in a sample of waste sulphite liquor\* were exchanged for hydrogen ion on a Dowex 50 column. Exchangeable anions were exchanged for hydroxyl ion on a Dowex 2 column. Completeness of removal of exchangeable ions was checked by repeated percolation of 500 ml. of solution through resin beds of both kinds and acidimetric analysis. The solution of ligninsulphonic acids so obtained was 0.105 *N* with respect to hydrogen ion.

All experiments were conducted using resin columns of 11 mm. diameter. A constant flow rate of 0.15 ml. per minute per ml. of resin bed was maintained throughout.

### *Cation-exchange Resin Regeneration*

A column of Dowex 50 in the hydrogen form 105 mm. height and 10.0 ml. volume was prepared. The resin in the sodium form was regenerated with 0.105 *N* sulphuric acid solution and 0.105 *N* solution of ligninsulphonic acids. Various volumes of acid solution were allowed to percolate through the column, the effluent from the column was collected in 20 ml. portions and analyzed. The column was washed and the regenerated capacity was determined by percolation of 2 *N* sodium chloride solution through the column and acidimetric analysis of the effluent. The data obtained are given in Figs. 1 and 2.

### *Mixed Bed Regeneration*

A column of 10 ml. of Dowex 50 in the hydrogen form and 15 ml. Dowex 2 in the hydroxide form was prepared. Height of the column was 265 mm. The

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Contribution from the Department of Chemical Engineering, University of Toronto, Toronto, Ontario. With financial assistance received through the School of Engineering Research, University of Toronto.

\* Fermented waste sulphite liquor supplied by the Ontario Paper Company, Ltd., Thorold, Ontario.

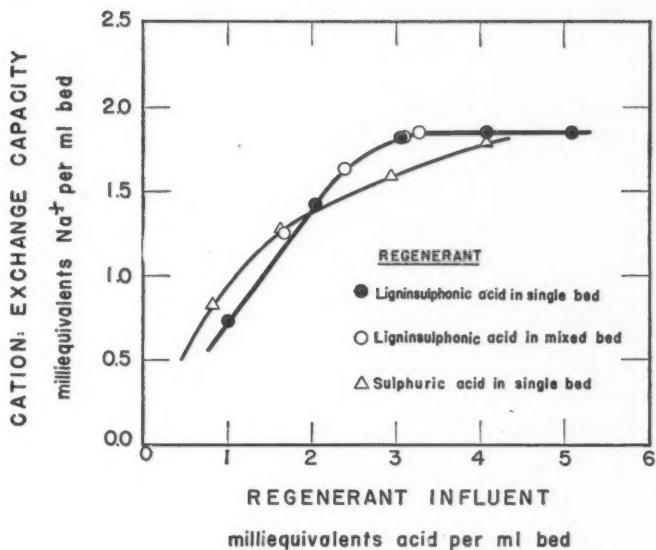


FIG. 1. Regeneration levels.

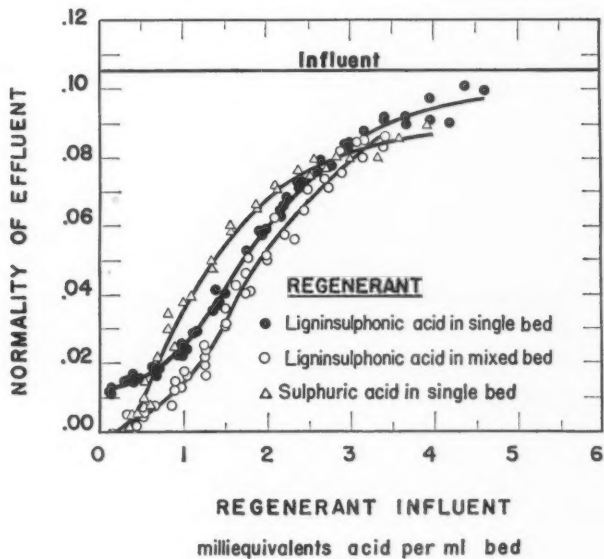


FIG. 2. Leakage data.

capacity of the bed for both the anion and the cation was determined as follows.

The bed was exhausted with 2 *N* sodium chloride solution. The acid normality of the effluent was determined and by exchange of the sodium ion in an aliquot for hydrogen ion the total anion concentration of the aliquot was determined acidimetrically. The anion-exchange resin in the mixed bed was regenerated with 10 times the equivalent amount of 1 *N* sodium hydroxide solution and was thoroughly washed with water. The cation-exchange resin in the bed was regenerated with various volumes of ligninsulphonic acid solution. The anion capacity of the bed after this regeneration was 0.70 milliequivalents per ml. of bed.

The data for regeneration and leakage are plotted in Figs. 1 and 2. It may be seen, that though the regeneration data for ligninsulphonic acids on a single bed and a mixed bed are very similar, the leakage for mixed bed is much lower than that for a single bed. In order to determine whether this difference might be accounted for by exchange of acid constituents on the anion-exchange resin the extent of such an exchange was investigated.

#### *Exchange on an Anion-exchange Resin*

Ten milliliter portions of ligninsulphonic acid solution were passed through an 8 ml. column of Dowex 2 in the hydroxide form. After each portion the bed was washed. The extent of exchange was determined by acidimetric analysis of effluent and washings. The procedure was repeated using a 16 ml. column of Dowex 2. Two runs were also made using sodium ligninsulphonate

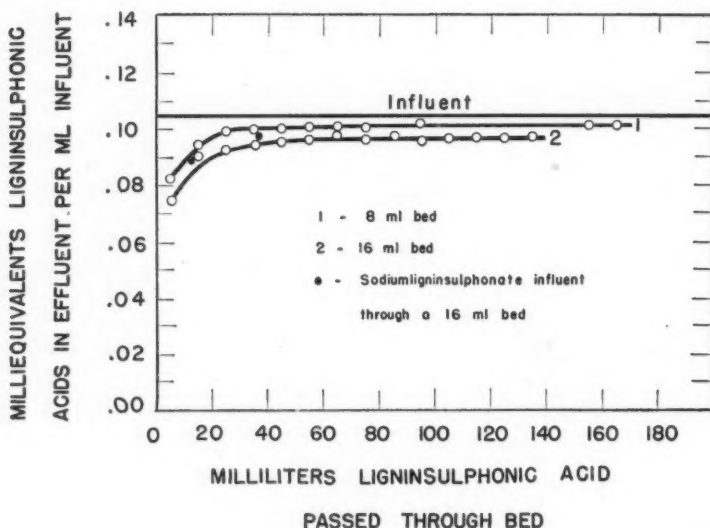


FIG. 3. Anion exchange.



solution as influent. The hydroxyl ion in the effluent was determined by titration and the ligninsulphonate concentration calculated on the assumption that the only process occurring was ion exchange. The resins used in these experiments were regenerated with sodium hydroxide solutions and the original capacities obtained.

These data indicate that some constituents of the ligninsulphonic acid solution are exchanged slowly on the anion-exchange resin. The correlation between this exchange and the leakage data is given below:

Volume of ligninsulphonic acid solution influent, ml.	Difference in leakage of a single bed and a mixed bed Fig. 2, m.e.	Calculated from Fig. 3, m.e.
100	1.5	1.4
200	2.6	2.2
300	3.5	3.0

Samuelson (2) has reported that there is a slow adsorption of constituents from waste sulphite liquors on anion exchange resins. His analysis of these constituents indicates that they are essentially carboxylic acids. Thus the high initial leakage on the cation-exchange bed is considered to be largely the result of carboxylic acid constituents which in the mixed bed column are exchanged on the anion exchange resin.

#### CONCLUSION

The data show that waste sulphite liquor may be used to regenerate mixed bed ion-exchange columns without separation of the resins.

#### ACKNOWLEDGMENT

The authors gratefully acknowledge the financial aid which was received through the School of Engineering Research of the University of Toronto.

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1. DEUEL, H., ANYAS-WEISZ, L., SOLMS, J. *Experientia*, 7: 294. 1951.
2. SAMUELSON, O. *Svensk Papperstidn.* 46: 583. 1943.

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## NOTE

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### EXAMINATION OF FLAWS IN GALVANIZED DOMESTIC HOT WATER TANKS<sup>1</sup>

BY D. CAPLAN AND P. J. SEREDA

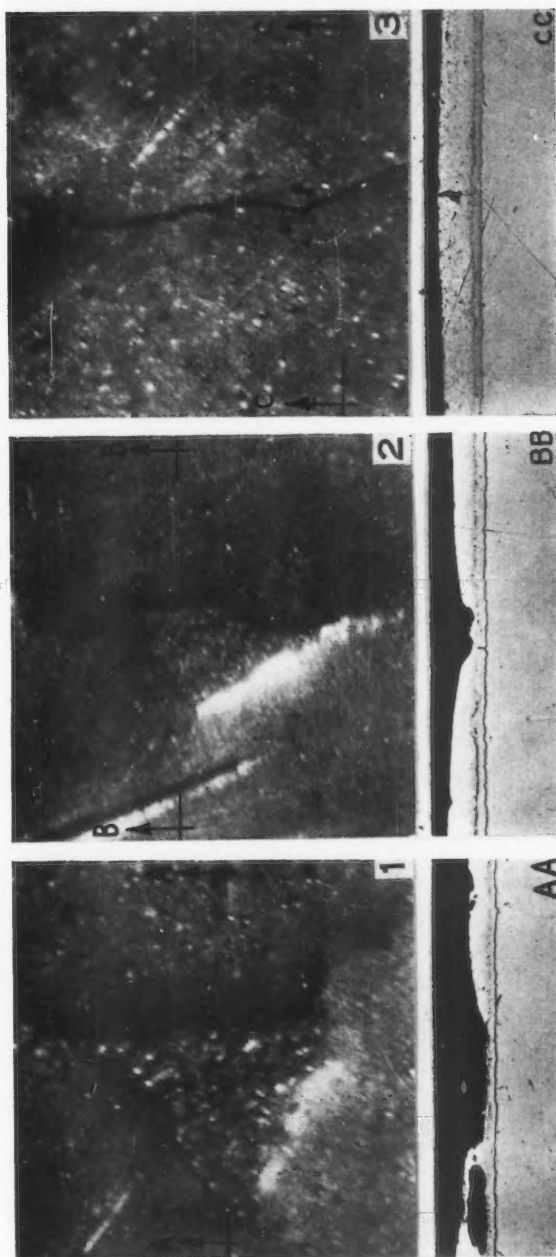
In some Canadian municipalities galvanized domestic hot water tanks had been found to fail by corrosion after a very short service life (3). In the examination of a large number of these "failed" tanks it was frequently observed that, where three zinc spangles met at a point, there was what appeared to be a bare spot or flaw in the zinc coating. These holes were up to about 0.5 mm. in diameter and, generally, were larger the heavier the gauge of the base steel. Another type of flaw frequently observed was a crack at the boundary between two spangles. The examination was necessarily carried out on the outer or uncorroded side of the tanks but it was assumed that the internal coatings would have had similar defects as manufactured. It was decided to investigate the structure of these flaws to determine whether tank failures might not have initiated at such points.

Samples containing typical flaws were cut from two 30-gal. tanks which had developed leaks after 17 months' use. Plan view photographs were taken, after which metallographic cross sections through the center of the defect were prepared.

Figs. 1, 2, and 3 show the results obtained. The plan view is shown as the upper photograph in each figure. The lower photograph shows the cross section at the same magnification (50 $\times$ ). The plane of the section is as indicated on the plan view. It can be seen that the flaws exist only in the outer pure zinc layer (the  $\eta$  phase), that the steel is not bare but is still covered by the iron-zinc alloy layers.

Since the zinc coating on galvanized sheet normally is anodic to steel it protects the underlying metal by corroding sacrificially. A small break in the coating, therefore, ordinarily does no harm because the surrounding zinc protects the exposed steel. It has been observed, however, that under some conditions of temperature and water composition, a polarity reversal takes place between zinc and iron with the iron then being the anode (1, 2). Since the metallographic sections show that the steel is not exposed at the bottom of the flaws, such a polarity reversal would increase the corrosion rate at these areas only if the alloy layers as well as the base metal became anodic to the  $\eta$  phase. In the absence of polarity reversal, premature failure may result from the fact that the galvanized coating is thinnest at the flaws and that steel becomes exposed there before sufficient time has elapsed for the calcareous protective layer to be established.

<sup>1</sup>Issued as N.R.C. No. 3021.



FIGS. 1-3.

1. GILBERT, P. T. Pittsburgh Intern. Conf. on Surface Reactions. Corrosion Publishing Company, Pittsburgh. 1948. pp. 21-49.
2. HUXENG, R. B. Corrosion, 6: 308-312. 1950.
3. SEREDA, P. J., THOMAS, W. R., and COHEN, M. Can. J. Technol. 29: 435-446. 1951.

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